Reflection high energy electron diffraction observation of exchange reaction dynamics on InAs surfaces

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We have used time-resolved reflection high energy electron diffraction (RHEED) measurements to study the dynamics of a surface, anion exchange reaction. In the experiment, InAs surfaces are exposed to Sb_x fluxes and subsequent changes in the crystals' RHEED patterns are examined. We find that when an InAs surface is initially exposed to an Sb flux the specular spot intensity first decreases, then recovers back toward its initial value. The shape of the intensity versus time curves is extremely reproducible if the absolute Sb flux and the Sb species are kept constant. The length of time required for the RHEED pattern to stabilize is much shorter for cracked Sb than for uncracked Sb. The RHEED dynamics are also faster if the total Sb flux increases. The behavior of the RHEED dynamics as a function of Sb flux and Sb species is consistent with the changes in the RHEED pattern being due to an Sb/As exchange reaction on the crystals' surface. The RHEED data are compared to previously published x-ray photoelectron spectroscopy (XPS) data which studied exchange reactions on InAs surfaces exposed to Sb fluxes. The XPS study confirmed that the incident Sb did indeed exchange with As in the epilayer and estimated the exposure time needed to complete the Sb/As exchange reaction. The time scales for exchange associated with the RHEED and XPS data are in good agreement, which further indicates that the observed RHEED dynamics are due to the Sb/As exchange reaction. Preliminary results from exposing GaSb surfaces to As fluxes show similar RHEED and XPS behavior. This suggests that RHEED could be generally applicable to the study of surface exchange reaction dynamics.

Reflection high energy electron diffraction (RHEED) has long been used for *in situ* surface studies. It is a particularly powerful tool in molecular beam epitaxy (MBE) growth reactors since the ultrahigh vacuum environment and RHEED geometry allow examination of diffraction patterns during crystal growth. Among the current uses of RHEED are growth rate determination,[1,2] study and control of alloy composition and layer thicknesses in quantum well and superlattice structures,[3,4] studies of dopant incorporation,[5] and measurements of surface diffusion lengths.[6,7] More recently, RHEED systems have been used as both scanning electron microscopes[8] and electron microprobes.[9] In addition, RHEED is routinely used by MBE operators to determine changes in the surface reconstruction of samples. These well-defined reconstruction changes can be used to calibrate substrate temperatures and determine the flux ratios incident on the sample. In this work we report the observation of surface exchange reaction dynamics using RHEED.

We find that when an InAs surface is exposed to an Sb flux (Sb/InAs), the intensity of the specular reflection in the RHEED pattern initially decreases then recovers toward its initial value. The time needed for the RHEED pattern to stabilize after starting the Sb exposure is extremely reproducible as long as the absolute Sb flux and the temperature of the Sb cell's cracking zone are held constant. The stabilization time (ST) is much shorter when using a beam of cracked Sb (consisting mainly of Sb_2 with some Sb) as opposed to a beam of uncracked Sb (composed exclusively of Sb_4).[10] Increasing the absolute Sb flux also decreases the ST of the diffraction pattern. The RHEED data are compared to a previously published x-ray photoelectron spectroscopy (XPS) study of the effect of Sb/InAs exposures.[11] This study confirmed that a self-limiting exchange reaction between the incident Sb, and As in the epilayer (Sb/As) does occur during Sb/InAs exposures. The XPS data were used to determine the Sb dose needed to complete the Sb/As exchange reaction. The exchange times obtained from the XPS experiments are in good agreement with the ST from the RHEED patterns. The effect on the ST of varying the Sb flux and Sb species as well as the good agreement between the XPS and RHEED data are consistent with the conclusion that the temporal changes in the RHEED intensity are due to the Sb/As exchange reaction. If so, then RHEED can be used to indirectly probe exchange reaction dynamics on crystal surfaces.

The samples studied were grown in a Perkin–Elmer 430 molecular beam epitaxy system equipped with cracked Sb and As sources at a substrate temperature of ~385 °C. This temperature was chosen to match the conditions used when growing InAs/GaInSb long wavelength infrared detectors.[12] The samples consisted of InAs layers, at least 100 Å thick,

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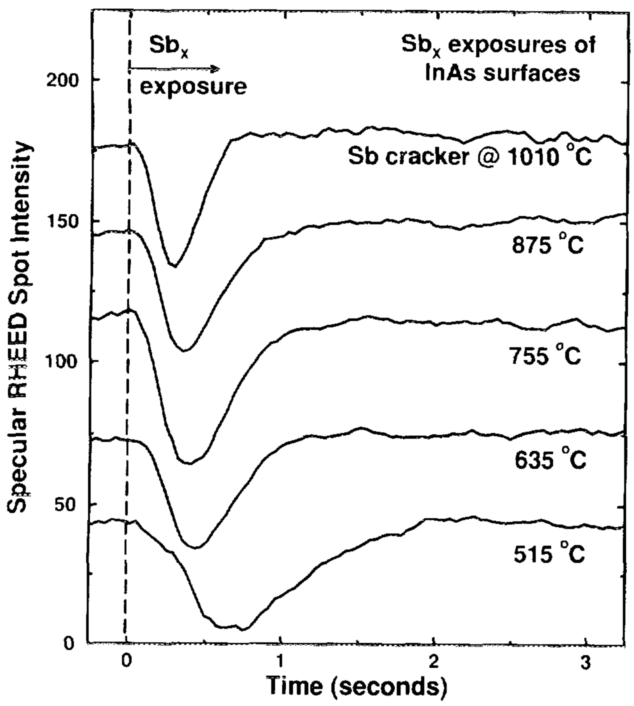

FIG. 1. Plots of the change in the specular RHEED spot intensity during Sb/As exchange reactions. The dashed vertical lines denote when the InAs surfaces are first exposed to an Sb_x flux. The curves are vertically offset for clarity. The lower curve was obtained by exposing an InAs surface to an Sb_4 flux. In the upper curve the beam consisted mainly of Sb_2 with some Sb. In the middle curves an intermediate Sb flux composition was used. Each data set is labeled with the nominal cracking temperature used.

grown on relaxed InAs buffer layers, deposited on (100) GaAs substrates. The InAs epilayers were exposed to only an Sb flux. Two sets of samples were sequentially prepared for RHEED and XPS analysis. Throughout all of the Sb exposures, the RHEED pattern remained streaky, with the surface reconstruction changing from 2×4 to 1×3 for sufficiently large Sb doses.

The RHEED measurement consisted of videotaping the diffraction pattern on the (110) azimuth while exposing an InAs surface in Sb. The video signal was then digitized into a 640×480 array of single-byte data. A computer program tracked and recorded changes in the intensity and width of the specular spot during the Sb exposures. The system can record between 25 and 50 data points per second. Following this, the surface was buried under an ~100 Å InAs layer and an XPS sample was prepared.

For the XPS measurements, a series of InAs epilayers were exposed to either cracked or uncracked Sb fluxes. The length of the Sb exposures varied from 2 s to 15 min. These samples were transferred under UHV to an analysis chamber, where XPS was used to study the energies and relative intensities of the In, Sb, and As core level peaks. From this it was possible to determine that Sb atoms did indeed exchange with As atoms in the InAs epilayers, and to estimate the extent of that exchange as a function of Sb exposure time.[11]

In Fig. 1 we plot the measured change in specular spot intensity of the RHEED pattern during an Sb/InAs exposure. The data were taken with the cracking zone of the Sb effusion cell at different temperatures. We estimate that for the bottom curve the Sb flux consisted entirely of Sb_4 while for the top curve the Sb flux was predominantly Sb_2 with some Sb.[10] The Sb beam composition monotonically changes between these two extremes. The start of the Sb exposure is denoted by the dashed vertical line and the data are vertically offset for clarity. The substrate temperature and total Sb flux were held constant for all the data shown. The curves in Fig. 1 are qualitatively similar. In each of them the specular intensity decreases at the start of the Sb exposure then recovers back toward its initial value. The difference between the curves is the time needed for the specular spot intensity to stabilize after initiating the Sb/InAs exposure. From Fig. 1 it can be seen that the ST monotonically decreases as the cracking zone temperature increases. Based on the previous XPS study we know that an Sb/As exchange reaction occurs under these conditions. Further, physical intuition suggests that the exchange reaction will occur faster for a flux of either Sb or Sb_2 than for a flux of Sb_4, since Sb and Sb_2 should be more reactive than Sb_4. Also, assuming that the absolute Sb flux is held constant, cracking the Sb beam leads to higher Sb coverage of the InAs surface, and consequently a faster Sb/As exchange reaction. The behavior of the ST in Fig. 1 is consistent with the conclusion that the changes in the diffraction intensity are due to the Sb/As exchange.

Figure 2 shows the reproducibility of the data discussed above. The two panels show overlays of RHEED data taken over the course of about 6 weeks. The upper panel shows data taken while using a cracked Sb beam (mainly Sb_2) and the data in the lower panel was taken while using an uncracked Sb beam (Sb_4 flux). The dashed vertical lines indicate when the Sb exposure was started. Great care was taken to hold the substrate temperature and absolute Sb flux constant. Within each panel, the profiles of the intensity decreases are extremely similar in magnitude, shape, and duration. Most importantly, the ST is the same for the different curves. The only difference between the curves is the final value of the diffraction intensity which we believe is due to surface morphology and not the exchange reaction itself, though further work is necessary to confirm this.

We also looked at the effect of varying the bulk Sb cell temperature for fixed cracker temperatures. We found that the ST was inversely proportional to the bulk cell temperature. By comparing the ST to Sb vapor pressure tables we found that the ST scaled as one over the total Sb flux. This further indicates that the RHEED dynamics are characteristic of the Sb/As surface exchange reaction. The scaling behavior of ST, with respect to absolute Sb flux, also suggests that the Sb/As exchange reaction is limited by the arrival of Sb and not the exchange reaction rate.

In Fig. 3 we show a comparison of representative RHEED data from Fig. 2 with XPS measurements of the relative Sb coverage of InAs surfaces after various Sb exposure times. As can be seen from the data, the ST of the RHEED pattern corresponds quite closely with the time measured by XPS for the Sb/As exchange reaction to saturate, with the minimum in the RHEED temporal intensity profile corresponding to a fractional Sb coverage.

It has long been believed that Sb/InAs exposures cause a

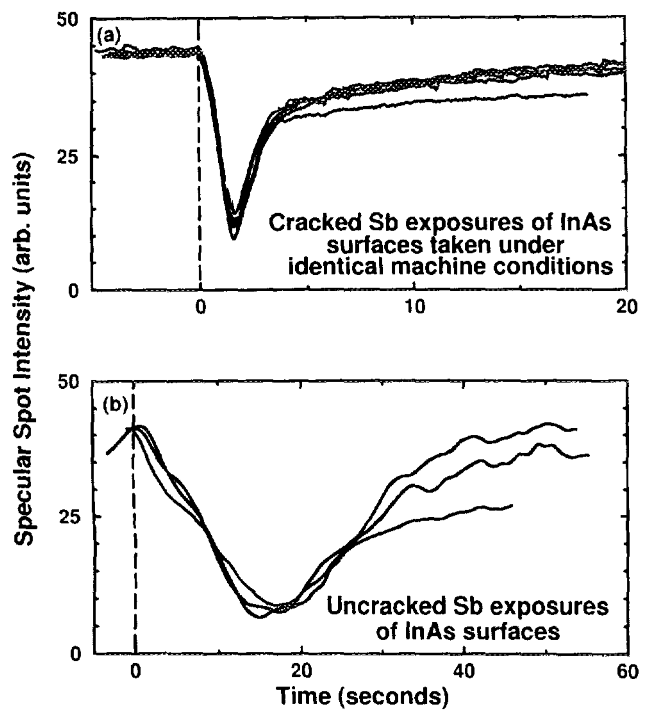

FIG. 2. Overlays of plots of the change in the intensity of the specular RHEED spot while the anion exchange reaction is occurring. The dashed vertical lines signify when the InAs surfaces are exposed to the Sb flux initiating the Sb/As exchange reaction. The upper panel shows data taken when the Sb flux was predominantly composed of Sb and Sb_2, while in the lower panel a beam composed exclusively of Sb_4 was used. The group of curves within each panel show several measurements of the exchange reaction taken under identical growth chamber conditions showing the reproducibility of the RHEED dynamics.

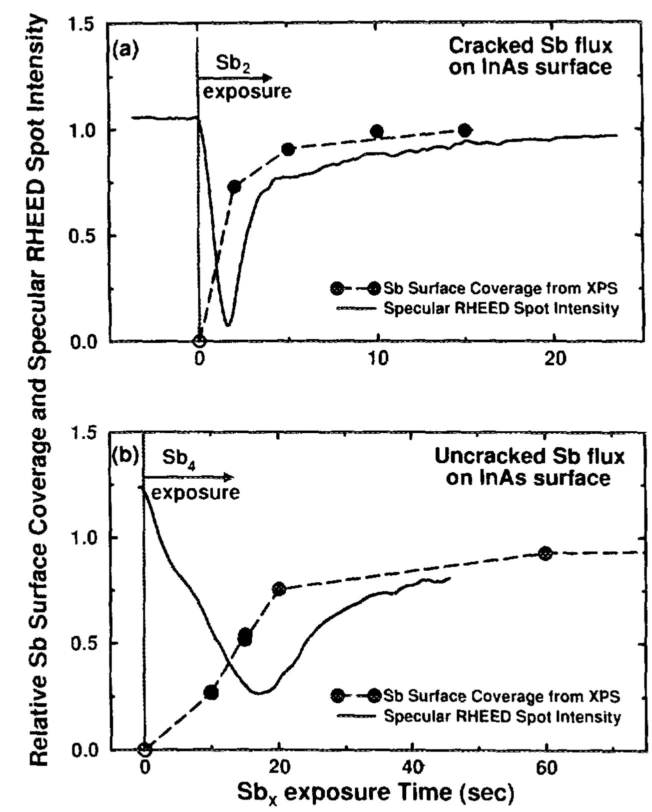

FIG. 3. A comparison of representative RHEED data from Fig. 2 and XPS measurements of relative Sb surface coverage of InAs surfaces exposed for a period of time to an identical Sb flux. Each RHEED data curve is representative of a series of data sets taken immediately prior to preparing a surface for an XPS measurement. The timescales on which the RHEED dynamics occur and Sb surface coverage changes are very similar. This indicates that the changes in the RHEED specular spot are related to the Sb/As exchange reaction.

surface, anion exchange reaction. This was based on the fact, that after the Sb exposure the surface showed a 1×3 reconstruction which is indicative of InSb. The previously reported XPS experiment confirmed this intuition, and showed that the Sb/As exchange reaction is self-limiting. It is also believed that forming this layer of In–Sb bonds when depositing Sb based materials onto InAs leads to improved device performance.[12–14] The result presented here, goes beyond the previous RHEED result which was based on recognition of surface reconstructions. By monitoring the specular spot intensity, it is now possible to probe the dynamics of the Sb/As exchange reaction. Preliminary studies of GaSb surfaces exposed to an As flux (As/GaSb) give similar results. While the RHEED intensity dynamics for this system are very different from the Sb/InAs system, their dependence on growth conditions and correlation to preliminary XPS data suggest that exchange reaction dynamics in the As/GaSb system can also be monitored with RHEED. Taken together, the Sb/InAs and As/GaSb results suggest that this technique could be used to study the dynamics of a wide range of surface exchange reactions.

As shown in Fig. 3, the minimum in the RHEED temporal intensity profile corresponds to a fractional Sb coverage. This suggests that the change in the RHEED intensity during the Sb exposure could be due to a mechanism similar to that believed to cause RHEED oscillations during MBE growth: temporal modulation of the surface roughness.[15,16] A possible cause of the surface "roughness" could be the stoichiometry of the surface. At the start of the Sb exposure As will cover the crystal surface (with the growth conditions employed). By the time the RHEED pattern stabilizes, the XPS measurements show that Sb is the dominant surface species. Since the form factors for electrons scattering from Sb and As differ, this chemical roughness could act like the "surface roughness" used to explain RHEED intensity oscillations during MBE growth. Another interpretation of the data is that the RHEED dynamics are simply a result of a surface phase change, with the intensity data characteristic of a first order phase change.

In conclusion, we have used RHEED to explore the dynamics of a surface exchange reaction. We find that the specular intensity drops sharply at the start of the Sb/InAs exposure, then recovers toward its initial value. The time needed for the diffracted intensity to stabilize is a strong function of the Sb species incident on the InAs surface. The RHEED pattern stabilizes much faster for fluxes consisting primarily of Sb and Sb_2, than for incident fluxes consisting of Sb_4. We also find that the surface stabilizes faster when the absolute Sb flux is increased. Both of these behaviors are consistent with the conclusion that changes in the RHEED pattern are due to the Sb/As exchange reaction occurring on the InAs surface. We also compare the RHEED data to XPS measurements of the relative Sb coverage of InAs surfaces exposed to Sb for various times. The stabilization time of the RHEED pattern is in good agreement with the time indicated by the XPS measurements for the Sb/As exchange reaction to reach completion. This further suggests that the RHEED dynamics are caused by the Sb/As exchange reaction. Though further study is necessary to confirm this conclusion, the RHEED results indicate the possibility of indirect, time-resolved studies of surface exchange reaction and interface formation dynamics. This result could have a wide array of potential applications ranging from basic material science studies to MBE process control in manufacturing.

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